COMPLEX CATIONS IN MICROANALYSIS:

THE APPLICATION OF 2,2′-DIPYRIDYL, *ORTHO*-PHENANTHROLINE, AND NITRO-*ORTHO*-PHENANTHROLINE COMPLEXES IN THE MICROSCOPICAL DETECTION OF ANIONS

BY

PETER CHARLES MARKUNAS

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M.S., University of Illinois, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1940

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INTRODUCTION

During the past half century, microanalysis has been enriched with numerous microscopic tests for almost all of the cations. In marked contrast with this, there are few and in some cases no good microscopic tests for many of the anions. Since only a limited number of reactions are available for the identification of certain anions, there is great need of discovering new reagents for or adapting existing ones to the microscopical detection of these ions. This work was undertaken for that purpose.

HISTORICAL

Although complex salts have been recommended and used in numerous analytical procedures for many years, only a limited application has been made of this type of reagent for the precipitation and microscopic identification of anions. Behrens and Kley (1), who probably were the first to suggest the use of a complex cation for the analysis of an anion, and Chamot and Mason (2) proposed the use of hexamminocobaltic chloride (luteo cobaltic chloride) as a reagent for the differentiation of pyrophosphate ion from phosphate and phosphite ions. Hynes and Yanowski have recommended this same reagent for the detection and identification of other anions (3) and also proposed a series of similar reagents (4, 5, 6, 7) for the same purpose. It was Blau's work (8) that prompted Polucktov and Nazarenko to suggest the use of the complex salt of 2,2′-dipyridyl with ferrous sulfate as a reagent for the microchemical detection of a series of anions (9), and it was researches of both Blau and Polucktov and Nazarenko that suggested to the author that it is not improbable that the other complex salts, namely, those of *o*-phenanthroline and 2,2′-dipyridyl with cadmium, cobalt, copper, iron, nickel, and zinc, might be of equal or even greater sensitivity and applicability than the ferrous dipyridyl complex.

EXPERIMENTAL

Using 0.025 molar solutions of the complex salts of 2,2′-dipyridyl, *o*-phenanthroline, and nitro-*o*-phenanthroline with cadmium, cobalt, copper, iron, nickel, and zinc as reagents and 1% solutions (10 mg. of the anion per ml.) of the alkali metal salts of about eighty anions as test solutions, the applicability of these reagents for the microscopical detection of anions was determined.

It was found that: (a) The complex salts of *o*-phenanthroline and 2,2′-dipyridyl with iron, cadmium, zinc, and nickel were the most satisfactory reagents for this purpose. (b) All of the nitro-*o*-phenanthroline complex salts are so insoluble that almost always an amorphous precipitate is obtained whenever these latter reagents are treated with an anion. (c) Of the approximately eighty anions examined, about forty were found to yield characteristic crystalline products when treated with these reagents. (d) These crystalline products form readily and are sufficiently distinctive to be recognized by means of a microscope.

The technic used in the performance of the tests is as follows: A drop of the reagent solution was placed on a glass slide close to a drop of the test solution, but not touching it. By means of a drawn-out glass rod, a tiny channel is made to flow from the reagent drop into the test drop, the object slide being tipped slightly to facilitate flow. Care was taken not to rub the glass slide with the rod. Otherwise too rapid crystallization results. Any reaction taking place or crystal formation was observed immediately by means of a microscope. For immediate recording of the appearance of the precipitate, a Leitz microscope with an upright camera was used. Illumination was furnished by a Spencer standard voltage microscope lamp and photographs were taken on Wratten M plates to be used as permanent records.

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VITA

The author was born November 29, 1911, at Chicago, Illinois. He received his elementary education in several schools in the southern part of the state and was graduated from the Centralia Township High School in June, 1930. In September of the same year, he entered Shurtleff College, where in June, 1934, he completed the prerequisites required for his degree as a Bachelor of Science.

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